

2

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
<small>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</small>				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE March 1990	3. REPORT TYPE AND DATES COVERED Final 12-1-88 - 11-30-89	
4. TITLE AND SUBTITLE  DURIP Advanced Polymer Solid State NMR Instrumentation			5. FUNDING NUMBERS  61104D 3842 A2	
6. AUTHOR(S)  David M. Rice			7. PERFORMING ORGANIZATION  Univ of Massachusetts  Amherst, MA 01003	
8. PERFORMING ORGANIZATION REPORT NUMBER  90 - 0436			9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)  AFOSR/NC Building 410, Bolling AFB DC 20332-6448	
10. SPONSORING/MONITORING AGENCY REPORT NUMBER  AFOSR-89-0184			11. SUPPLEMENTARY NOTES	
12a. DISTRIBUTION/AVAILABILITY STATEMENT  APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The grant provided instrumentation which has been included within our Laboratory for the advanced Nuclear Magnetic Resonance study of polymers in the solid state. This equipment has made it possible to use this laboratory for the support of the grants cited in section IIa of our original proposal and above. The substantial majority of our initial, specific NMR objectives have been accomplished. These include the study of the <u>structure and morphology of Poly(p-phenylene vinylene) (PPV)</u> and the <u>Molecular Interactions in High Temperature Polymer Blends</u> . The instrumentation has provided experimental capability in two new areas which are being used generally in further work. In particular we have 1) implemented methods for the NMR study of the structure and orientation of high strength films and fibers. These methods are now being used for the study of PBZT fibers. 2) Two-dimensional NMR methods have been developed which provides for quantitative measurement of conformation and domain structure of blends. Two-dimensional NMR will be a major thrust of future NMR blends experiments.				
14. SUBJECT TERMS			15. NUMBER OF PAGES 8	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT SAR	

FINAL REPORT

RESEARCH EQUIPMENT: URIP Grant

AFOSR

Grant AFOSR 89-0184

1 December 1988 - 30 November 1989

David M. Rice  
Polymer Science and Engineering  
University of Massachusetts  
Amherst, MA 01003

Approved for public release;  
distribution unlimited.

### ACKNOWLEDGMENT

The Principal Investigator would like to express his sincere thanks to Dr. Donald L. Ball, Director of Chemical Sciences, Air Force Office of Scientific Research, to Dr. Donald R. Ulrich, Senior Program Manager, Directorate of Chemical Sciences, and to other members of the Directorate for their unfailing cooperation, help and courtesy extended to him during the period of this contract.

Accession For	
NTIS GRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	



CONTENTS

- I. Title
- II. Principal Investigator
- III. Contract Number
- IV. Dates
- V. Senior Research Personnel
- VI. Junior Research Personnel
- VII. Abstract of Accomplishments
- VIII. Description of Research Undertaken
- IX. Publications

- I. TITLE: Research Equipment: URIP Grant
- II. PRINCIPAL INVESTIGATOR: Dr. David M. Rice  
Polymer Science and Engineering  
University of Massachusetts  
Amherst, MA 01003
- III. CONTRACT NUMBER: AFOSR 89-0184
- IV. DATES: 1 December 1988 - 30 November 1989
- V. SENIOR RESEARCH PERSONNEL: None
- VI. JUNIOR RESEARCH PERSONNEL: None

## VII. ABSTRACT OF ACCOMPLISHMENTS

The grant provided instrumentation which has been included within our Laboratory for the advanced Nuclear Magnetic Resonance study of polymers in the solid state. This equipment has made it possible to use this laboratory for the support of the grants cited in section IIa of our original proposal and above. The substantial majority of our initial, specific NMR objectives have been accomplished. These include the study of the structure and morphology of Poly(p-phenylene vinylene) (PPV) and the Molecular Interactions in High Temperature Polymer Blends. The instrumentation has provided experimental capability in two new areas which are being used generally in further work. In particular we have 1) implemented methods for the NMR study of the structure and orientation of high strength films and fibers. These methods are now being used for the study of PBZT fibers. 2) Two-dimensional NMR methods have been developed which provides for quantitative measurement of conformation and domain structure of blends. Two-dimensional NMR will be a major thrust of future NMR blends experiments.

## VIII. DESCRIPTION OF RESEARCH UNDERTAKEN : EXAMPLES

### Structure and Morphology of Poly(p-phenylene vinylene) (PPV).

The simulation of deuterium quadrupole echo NMR spectra has provided data which support an empirical two component Gaussian distribution of crystallite orientations in phenylene deuterated and vinylene deuterated PPV. The observed distribution is similar to the Kratky distribution predicted for pseudo-affine deformation, and for large draw ratios, the orientation function is somewhat less than that usually obtained from infrared measurements with protonated films. In general a direct comparison of infrared dichroism data and NMR data has benefited the interpretation of both methods.

Spectra show evidence of phenylene ring tilt relative to the crystallite *c* axis. The tilt angle ( $7.7^\circ$ ) is less than the  $9.2^\circ$  predicted for a stilbene like structure. the smaller tilt provides evidence for chain disorder within PPV crystallites.

NMR spectra provide a method to measure the rate of  $180^\circ$  rotational jumps of the phenylene rings of PPV about their 1,4 axes. The rotational jump rate is related to the double character of the phenylene-vinylene single bonds of PPV and has been shown to be affected by doping. NMR spectral shapes may be related to the conjugation length and NMR studies of doped PPV are now in progress.

Characterization of the  $^{13}\text{C}$  CPMAS spectra of PPV have yielded a complete assignment. A new two dimensional  $^{13}\text{C}$  CPMAS method has been

developed and implemented in this laboratory. This method will allow direct study of the structure and conformation of PPV and its substituted analogues. These materials have shown promise as NLO polymers. The goal of future work will be to relate conformation, determined by NMR, to the observed 3rd order susceptibility.

The deuterium and  $^{13}\text{C}$  NMR methods developed to study the conformation and orientation of PPV have been extended to the study of a new polymer, oriented films and fibers of poly(1,4-phenylene bis thiazole) (PBZT). Initial deuterium NMR experiments confirm the expected  $0^\circ$  tilt angle of the phenylene ring of PBZT. A study of the chain orientation distribution of PBZT is in progress and data will be compared with previous X-ray and infrared results. In general the capability for the NMR study of oriented polymers is a unique asset of this laboratory.

#### Molecular Interactions in High Temperature Polymer Blends

Solid State  $^{13}\text{C}$  CPMAS NMR has been employed to study the molecular basis of the miscibility of polybenzimidazole (PBI) and several polyimides (PI). An obvious interaction is the presence of a hydrogen bond between the N-H moiety of PBI and the carbonyl group of PI. This hydrogen bonding has been detected directly by NMR through the observation of a change in the  $^{13}\text{C}$  CPMAS lineshape of the carbonyl group of PI. The carbonyl line of PI broadens to greater chemical shift in PBI/PI blends. NMR data are directly comparable with FTIR data, and the fractions of interacting groups determined by each method are in qualitative agreement.



Deuterium quadrupole echo line shape data have provided new information about molecular interactions in miscible blends of polyimides (PI) and a deuterium labelled polyethersulfone (PES-d). The phenylene rings of PES-d have been shown to undergo rapid  $180^\circ$  rotational jumps. The jump rate distribution has been examined by deuterium NMR and found to be independent of blend composition and to show no relationship with mutual glass transition temperature of the blend. These data have suggested that the jump mechanism is determined by very local conformation, and is not the result of the low frequency dynamics associated with the glass transition. We have also observed similar behavior for the phenyl rings of polystyrene in blends of polystyrene and poly(2,6-dimethyl phenylene) oxide and suggest that this is a general phenomena in miscible blends.

High temperature deuterium spectra have been obtained for PI/PES-d blends in the vicinity of the glass transition and deuterium NMR spectra realize a sensitive measurement of concentration inhomogeneity within miscible blends. Above the glass transition temperature, deuterium spectra collapse to a single narrow line due to the onset of chain motion. We have found that PES-d shows a broad distribution of motional onset temperatures beginning at the glass transition of the more mobile component and this distribution reflects concentration inhomogeneity within these blends. In contrast, PS/PPO blends, show a single onset temperature for molecular motion which coincides with calorimetric glass transition.

A new method has been developed to obtain two-dimensional  $^{13}\text{C}$ - $^1\text{H}$  correlation NMR spectra of blends. This method is based upon a selective cross-polarization between  $^1\text{H}$  and  $^{13}\text{C}$ , and offers the

opportunity to directly measure the number-average distance between mutually interacting segments of miscible blend components in the glassy state. Two-dimensional spectra have been obtained for pure PPO and for blends between PPO and polystyrene. These spectra have provided data which indicates that adjacent phenylene rings of pure PPO are approximately perpendicular and that this conformation does not change in a 50/50 blend. Two dimensional NMR data also indicate the lack of a specific interaction between the phenyl rings of polystyrene and the methyl groups of PPO as previously suggested.

The two-dimensional NMR methods under development in this laboratory are a major new capability and provide for quantitative measurement of the domain structure of polymer blends. Two dimensional experiments will be an important component of future NMR blends work and will include the study of conformational interactions in copolymer blends and further study of the specific interactions of polyimide blends.

## IX. PUBLICATIONS

None

The URIP equipment has been operational for 6-9 months. A very large number of publications in blends of conducting polymers coming to our group will to some extent be made possible by this apparatus.